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(54) Title: PROCESS FOR THE EPOXIDATION OF OLEFINS

(57) Abstract: The invention described herein relates to a process for the catalytic epoxidation of olefins with hydrogen peroxide in a continuous flow reaction system, wherein a gaseous phase containing an olefin and a liquid phase containing the hydrogen peroxide is present in the reaction system and the gaseous phase flows in countercurrent to the liquid phase.

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## PROCESS FOR THE EPOXIDATION OF OLEFINS

## Prior Art

5 From EP-A 100 119 it is known that propene can be converted by hydrogen peroxide into propene oxide if a titanium-containing zeolite is used as catalyst.

Unreacted hydrogen peroxide cannot be recovered economically from the  
10 epoxidation reaction mixture. Furthermore, unreacted hydrogen peroxide involves additional effort and expenditure in the working up of the reaction mixture. The epoxidation of propene is therefore preferably carried out with an excess of propene and up to a high hydrogen peroxide conversion. In order to achieve a high hydrogen peroxide conversion it  
15 is advantageous to use a continuous flow reaction system. Such a reaction system may comprise either one or more tubular flow reactors or an arrangement of two or more flow mixing reactors connected in series. Examples of flow mixing reactors are stirred tank reactors, recycle reactors, fluidised bed reactors and fixed bed reactors with recycling  
20 of the liquid phase.

In order to achieve a high reaction velocity as high a propene concentration as possible in the liquid phase is necessary. The reaction is therefore preferably carried out under a propene atmosphere  
25 at elevated pressure.

The decomposition of hydrogen peroxide with the formation of molecular oxygen always occurs to a slight extent as a secondary reaction on the titanium silicalite catalyst. In order to be able to operate the  
30 epoxidation process reliably on an industrial scale the oxygen that is formed must be removed from the reaction system. This is effected most simply by flushing the oxygen out with a propene waste gas stream.

EP-A 659 473 describes an epoxidation process that combines these features. In this connection a liquid mixture of hydrogen peroxide, solvent and propene is led over a succession of fixed bed reaction zones connected in series, wherein the liquid phase is removed from each reaction zone, is led over an external heat exchanger to extract the heat of reaction, and the major proportion of this liquid phase is then recycled to this reaction zone and a minor proportion of the liquid phase is passed to the next zone. The individual reaction zones behave as flow mixing reactors on account of the liquid recycling over the fixed bed. At the same time gaseous propene is fed in together with the liquid feed stock mixture, is guided in a parallel stream to the liquid phase over the fixed bed reaction zones, and is extracted at the end of the reaction system in addition to the liquid reaction mixture as an oxygen-containing waste gas stream. Although this reaction procedure enables the propene oxide yield to be raised compared to conventional tubular reactors without the temperature control described in EP-A 659 473, it nevertheless involves considerable additional costs on account of the complexity of the reaction system required to carry out the process. Furthermore, the described raised yield can only be realised if the propene oxide contained in the waste gas stream is recovered. This necessitates an additional process stage, which in turn adds further to the costs of the process.

The object of the present invention is accordingly to provide a simple inexpensive process for the epoxidation of olefins with hydrogen peroxide, with which high conversions can be achieved combined with a high product yield and which can be carried out using conventional reaction systems.

## Subject of the Invention

This object is achieved by a process for the catalytic epoxidation of olefins with hydrogen peroxide in a continuous flow reaction system wherein a gaseous phase containing an olefin and a liquid phase containing the hydrogen peroxide are present in the reaction system and the gaseous phase is fed in countercurrent to the liquid phase.

An important advantage of the countercurrent arrangement according to the invention is the reduction in the amount of propene oxide that is discharged from the reaction system together with the oxygen-containing propene waste gas stream, and the resultant decreased expenditure on recovering propene oxide from this waste gas stream. As small a loss of propene oxide as possible is desired in order to achieve a high product yield according to the invention.

The countercurrent arrangement according to the invention of gaseous olefin and liquid reaction mixture in the reaction system may be accomplished in various ways depending on the chosen reaction system. In this connection reaction systems are suitable in which there is no complete back-mixing relative to the overall system, i.e. reaction systems whose residence time spectrum exhibits a maximum, or reaction systems involving plug flow.

If the epoxidation of olefins is carried out in a tubular flow reactor, then the gas stream containing the olefin is guided in countercurrent to the liquid phase within the reactor. In this connection the liquid stream is preferably led from the top downwards through the reactor, while the olefin flows from the bottom upwards through the reactor in the form of a gas stream. The reactor may be operated as a bubble column with a continuous liquid phase, as well as a trickle reactor with a continuous gas phase. The catalyst may be employed either as a

suspension in the liquid phase or in the form of a fixed bed, wherein the fixed bed may be designed both as a random catalyst packing as well as an ordered packing of coating monoliths or distribution bodies.

Preferably a tubular flow reactor is used as a fixed bed reactor with a  
5 random catalyst packing and continuous liquid phase.

In order to be able to operate the process continuously when changing and/or regenerating the epoxidation catalyst, two or more tubular flow reactors may if desired also be operated in parallel or in series in the  
10 aforescribed manner.

If the epoxidation of olefins is carried out in a succession of two or more tubular flow reactors connected in series, the substance streams of liquid phase and gaseous phase within a flow reactor may be guided  
15 either in co-current or in countercurrent, the substance streams being guided in countercurrent between the tubular flow reactors.

In an alternative embodiment the reaction system may comprise several reactors connected in series that are chosen independently of one  
20 another from flow mixing reactors and tubular flow reactors, the substance streams of liquid phase and gaseous phase being guided in countercurrent between the reactors. For example, flow mixing reactors and tubular flow reactors may also be used in combination within the reaction system consisting of reactors connected in series. Preferably,  
25 in this connection one or more flow mixing reactors are connected in series with a final tubular flow reactor. The particular advantage of such a reaction system is that the heat of reaction can be particularly easily extracted from the flow mixing reactors in which the major proportion of the reaction turnover takes place. The use of a final  
30 tubular flow reactor ensures that the hydrogen peroxide conversion takes place as fully as possible. Stirred tank reactors, recycle reactors, jet reactors with liquid circulation, or fixed bed reactors with a

monomethyl ether, and ketones such as for example acetone or 2-butanone. Methanol is particularly preferably used as solvent.

The process according to the invention for the epoxidation of olefins, preferably propene, is carried out at a temperature of  $-10^{\circ}$  to  $100^{\circ}\text{C}$ , preferably at  $20^{\circ}$  to  $70^{\circ}\text{C}$ . The olefin is preferably employed in excess relative to the hydrogen peroxide in order to achieve a significant consumption of hydrogen peroxide, the molar ratio of olefin, preferably propene, to hydrogen peroxide preferably being chosen in the range from 1.1 to 10. When adding a solvent the amount of solvent is preferably chosen so that only a liquid phase is present in the reaction mixture. The solvent is preferably added in a weight ratio of 0.5 to 20 relative to the amount of hydrogen peroxide solution used. The amount of catalyst employed may be varied within wide limits and is preferably chosen so that a hydrogen peroxide consumption of more than 90%, preferably more than 95%, is achieved within 1 minute to 5 hours under the employed reaction conditions.

In a preferred embodiment of the process according to the invention propene is used that may contain between 0% and 15% of propane. Propene may be fed as a liquid as well as in gaseous form into the reaction system. The amount of propene that is fed in is chosen so that under the reaction conditions in the reactors a gas phase is formed consisting predominantly of propene, and so that from the first reactor of the reaction system a waste gas can be removed whose oxygen content lies outside the explosion limits for propylene-oxygen mixtures. The pressure in the reaction system is preferably chosen to be between 50% and 100% of the saturated vapour pressure of propylene at the reaction temperature.

The present invention will be illustrated hereinafter with the aid of figures and examples for the epoxidation of propene.

Fig. 1 shows a tubular flow reactor. Stream 1 denotes the feed stream of the liquid reaction phase, stream 2 denotes the outlet stream of the liquid reaction phase, stream 3 denotes the feed stream of the gaseous component, and stream 4 denotes the waste gas stream. These designations are also retained for the other figures.

Fig. 2 illustrates the flow of the substance streams for three reactors connected in series. The liquid feedstocks are fed with stream 1 into the first reactor. From the first reactor the liquid reaction mixture is led via the streams 5 and 6 into the second and third reactors and is removed in liquid form as stream 2 from the third reactor. Propene, optionally mixed with propane, is fed with the stream 3 into the third reactor and together with the streams 7 and 8 is led in gaseous form via the second reactor into the first reactor. From the first reactor a waste gas stream is removed via the stream 4, the waste gas stream containing, in addition to unreacted propene and possibly propane, the molecular oxygen formed by decomposition of hydrogen peroxide during the epoxidation reaction.

Fig. 3 shows by way of example a system consisting of three stirred tank reactors connected in series for the epoxidation using a suspension catalyst, wherein the system is operated according to the invention with countercurrent flow of liquid phase and propene gas, and the numbering of the substance streams agrees with Fig. 2.

When tubular flow reactors are connected in series, the flow of the substance streams within a reactor may take place both in countercurrent and in co-current.

Fig. 4 shows by way of example a system consisting of three fixed bed reactors connected in series with countercurrent flow within the

reactors, wherein the substance streams of liquid phase and propene gas flow in countercurrent between the reactors in the manner according to the invention.

5 Fig. 5 shows by way of example a system consisting of three fixed bed reactors connected in series with co-current flow within the reactors, wherein the substance streams of liquid phase and propene gas flow in countercurrent between the reactors in the manner according to the invention. In both diagrams the numbering of the individual substance  
10 streams agrees with Fig. 2.

Fig. 6 shows by way of example the combination of two stirred tank reactors with a bubble column reactor operating in co-current flow for the epoxidation using a suspension catalyst, the substance streams of  
15 liquid phase and propylene gas flowing in countercurrent between the reactors in the manner according to the invention. The numbering of the individual substance streams agrees with Fig. 2.

## 20 Example:

In an arrangement consisting of two stirred tank reactors and a tubular flow reactor with an overall volume of 6.25 litres, which are connected to one another corresponding to Fig. 6, 43 wt.% aqueous hydrogen  
25 peroxide solution is fed into the first reactor at a rate of 1045 g/h in parallel with a 2.0 wt.% suspension of titanium silicalite in methanol at a rate of 2630 g/h (stream 1). 1120 g/h of propene in gaseous form are fed at the same time from below into the third reactor (stream 5). The three reactors are thermostatically controlled at a temperature of  
30 65°C and the pressure in all three reactors is maintained at an excess pressure of 15.0 bar by means of a pressure retention valve on the first reactor. 215 g/h of unreacted propene with an oxygen content of 0.6



vol.% are removed at the pressure retention valve (stream 8). The hydrogen peroxide concentration is determined by redox titration and the contents of propene oxide, 1-methoxy-2-propanol, 2-methoxy-1-propanol and 1,2-propanediol are determined by gas chromatography at regular intervals in the liquid reaction mixture (stream 4) removed from the third reactor. When the stationary operational state has been reached the hydrogen peroxide conversion is 96.8%, the propene oxide yield referred to converted hydrogen peroxide is 90.3%, and the propene oxide selectivity, calculated as the ratio of the concentration of propene oxide to the sum of the concentrations of the products propene oxide, 1-methoxypropanol, 2-methoxypropanol and 1,2-propanediol, is 94.5%.

## Claims

1. Process for the catalytic epoxidation of olefins with hydrogen peroxide in a continuous flow reaction system, wherein a gaseous phase containing an olefin and a liquid phase containing the hydrogen peroxide is present in the reaction system, characterised in that the gaseous phase is guided in countercurrent to the liquid phase.
2. Process according to claim 1, characterised in that the reaction system is selected from one or more tubular flow reactors connected in series or in parallel.
3. Process according to claim 2, characterised in that the reaction system comprises several tubular flow reactors connected in series, the substance streams of liquid phase and gaseous phase flowing either in co-current or in countercurrent within a tubular flow reactor, and the substance streams flowing in countercurrent between the tubular flow reactors.
4. Process according to claim 1, characterised in that the reaction system comprises several reactors connected in series that are selected independently of one another from flow mixing reactors and tubular flow reactors, the substance streams of liquid phase and gaseous phase flowing in countercurrent between the reactors.
5. Process according to any of the preceding claims, characterised in that the catalyst is suspended in the liquid reaction phase.
6. Process according to any of claims 2 and 3, characterised in that the catalyst is used in the form of a fixed bed.

7. Process according to any of the preceding claims, characterised in that a titanium-containing zeolite is used as catalyst.
- 5 8. Process according to any of the preceding claims, characterised in that the olefin is propene.
9. Process according to claim 8, characterised in that a propene feed stream is used that in addition contains up to 15 vol.% of propane.

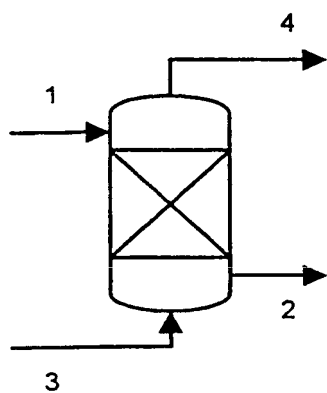
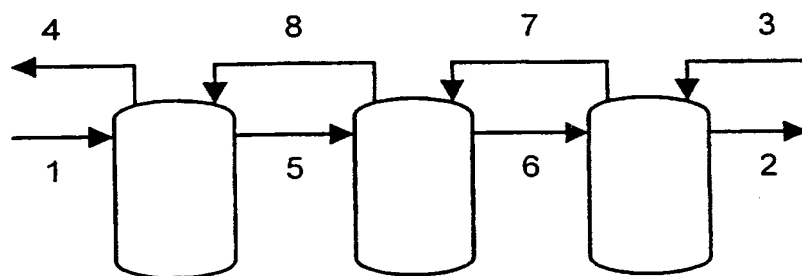


Fig. 1



5 Fig. 2

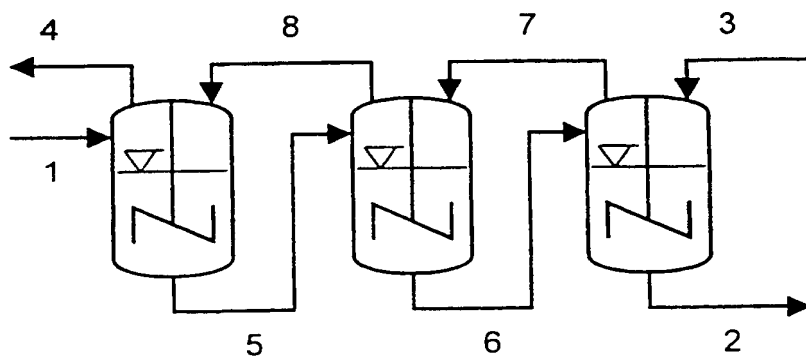


Fig. 3

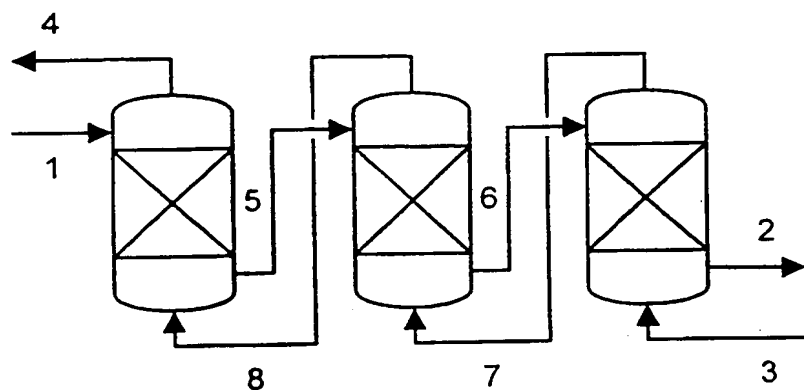
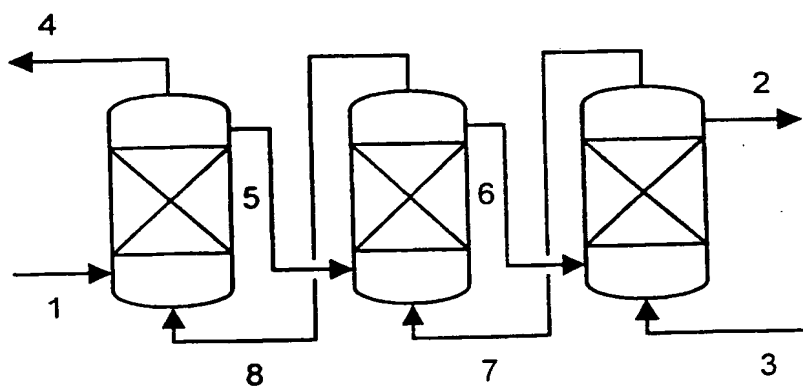


Fig. 4



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Fig. 5

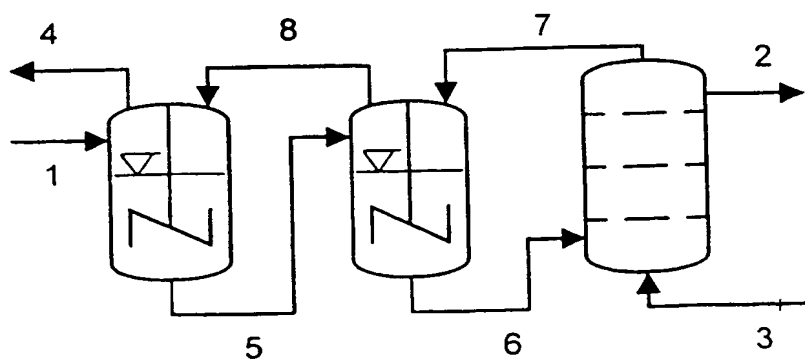


Fig. 6

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 01/01167

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D301/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 100 119 A (ANIC S.P.A.) 8 February 1984 (1984-02-08) cited in the application the whole document ---	1-9
A	EP 0 659 473 A (ARCO CHEMICAL TECHNOLOGY, L.P.) 28 June 1995 (1995-06-28) cited in the application the whole document -----	1-9

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